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(54) Title: LATE TRANSITION METAL COMPLEXES, THEIR USE AS CATALYSTS AND POLYMERS THEREFROM

(57) Abstract: The invention provides a novel metal complex which, when used with an activating cocatalyst, provides a novel catalyst composition. The invention also provides a polymerization method which utilizes the catalyst composition to produce polymers and copolymers containing polar monomer groups. More specifically, the invention comprises a composition comprising the formula $LMXZ_n$ wherein X is selected from the group consisting of halides, hydride, triflate, acetates, borates, C_1 through C_{12} alkyl, C_1 through C_{12} alkoxy, C_3 through C_{12} cycloalkyl, C_3 through C_{12} cycloalkoxy, aryl, thiolates, carbon monoxide, cyanate, olefins, and any other moiety into which a monomer can insert. M is selected from the group consisting of Cu, Ag, and Au. L is a nitrogen-containing bidentate ligand having more than two nitrogen atoms. Z is a neutral coordinating ligand and n equals 0, 1, or 2.

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LATE TRANSITION METAL COMPLEXES,
THEIR USE AS CATALYSTS AND POLYMERS THEREFROM

FIELD OF THE INVENTION

The invention is directed towards a late transition metal polymerization catalyst complex and its use in forming polymers from olefins or polar monomers and copolymers from olefins and polar monomers.

BACKGROUND

Polymers and copolymers may be formed from olefinic monomers by using transition metal catalyst technology. Ziegler-Natta catalysts have been used for many years while in more recent years metallocene catalysts have been preferred in certain applications since the polyolefins produced via metallocene catalysis often possess superior properties. The most well-known metallocene technology employs catalysts containing early transition metal atoms such as Ti and Zr.

Even though polyolefins formed by such metallocene catalysts possess certain enhanced properties over polyolefins produced by conventional Ziegler-Natta catalysts, further improvements in properties such as wettability and adhesiveness may be possible. It is believed that including polar monomers in an olefinic polymer or copolymer would improve these, and possibly other, properties. Unfortunately, polar monomers tend to poison early transition metal catalysts.

Certain late transition metal complexes such as those containing palladium and nickel, are more forgiving when incorporating certain polar monomers. However, most of these catalyst compositions are costly and

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produce highly branched polymers (e.g., 85-150 branches/1000 carbon atoms). Also, the functionalities are not in the chain but at the ends of branches. Consequently, they are limited to polar monomer contents to about 15 mol% or less. Another disadvantage of these compositions is that they incorporate only a limited number of polar monomers such as alkyl acrylates and vinyl ketones.

Recently, novel late transition organometallic catalysts have been made to address the aforementioned problems. More specifically, U.S. Patent 6,037,297 to Stibrany et al., herein incorporated by reference, details group 11 metal (Cu, Ag and Au) containing catalyst compositions having a pseudotetrahedral geometry that are useful in forming polymers and copolymers having hydrocarbyl polar functionality.

However, there is still a need to explore other group 11 metal complexes for use in polymerization processes. Ideally, these late transition metal complexes should be capable of forming olefinic polymers and copolymers containing polar monomers which are not highly branched, have polymer chain functionality and are capable of incorporating a wider variety of polar monomers.

SUMMARY

The instant invention provides a late transition metal complex which can be used with an activating cocatalyst to produce polymers and copolymers. Also, like the invention described in US Patent 6,037,297, the instant invention can be used to produce polymers and copolymers containing polar monomers.

In one embodiment, the invention is a composition having the formula $LMXZ_n$ wherein X is selected from the group consisting of halides, hydride,

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triflate, acetates, borates, C₁ through C₁₂ alkyl, C₁ through C₁₂ alkoxy, C₃ through C₁₂ cycloalkyl, C₃ through C₁₂ cycloalkoxy, aryl, thiolates, carbon monoxide, cyanate, olefins, and any other moiety into which a monomer can insert. M is selected from the group consisting of Cu, Ag, and Au. L is a nitrogen-containing bidentate ligand with more than two nitrogen atoms. Z is a neutral coordinating ligand and n equals 0, 1, or 2.

In another embodiment, the invention is a catalyst composition comprising the reaction product of: a metal complex having the formula $LMXZ_n$, as described above, and an activating cocatalyst. This embodiment of the invention is particularly useful in polymerization chemistry.

In yet another embodiment, the invention provides a method for using the composition to produce polymers and copolymers which contain polar monomer units. The method includes contacting the monomers under polymerization conditions with a catalyst composition comprising a composition having the formula $LMXZ_n$, as defined above, and an activating cocatalyst. Optionally, an oxidizing agent may also be employed during this process.

These and other features, aspects and advantages of the present invention will become better understood with regard to the following description and appended claims.

DESCRIPTION

The invention relates to a novel metal complex which, when used with an activating cocatalyst, provides a novel catalyst composition. The invention also provides a polymerization method which utilizes the catalyst composition.

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Generally speaking, the method of the invention produces polymers and copolymers containing polar monomer groups.

In one embodiment, the invention comprises a composition comprising the formula $LMXZ_n$ wherein X is selected from the group consisting of halides, hydride, triflate, acetates, borates, C_1 through C_{12} alkyl, C_1 through C_{12} alkoxy, C_3 through C_{12} cycloalkyl, C_3 through C_{12} cycloalkoxy, aryl, thiolates, carbon monoxide, cyanate, olefins, and any other moiety into which a monomer can insert; M is selected from the group consisting of Cu, Ag, and Au; L is a nitrogen-containing bidentate ligand with more than two nitrogen atoms; Z is a neutral coordinating ligand; wherein n equals 0, 1, or 2.

The geometric configuration of the metal complex of the instant invention can be either pseudotetrahedral or trigonal planar depending on the value of n (i.e., n can equal 0, 1 or 2). It should be appreciated by those skilled in the art that although the term "pseudotetrahedral" is used to describe the geometric structure of the metal complex, it does not exclude a pure "tetrahedral" geometrical arrangement. The prefix "pseudo" is used throughout the specification to most accurately describe the non-limiting embodiments described herein. Similarly, the term "trigonal planar" should be understood by those skilled in the art to also include geometric configurations which are approximately trigonal planar.

When the metal composition is reacted with an activating cocatalyst such as methyl alumoxane (a.k.a., "MAO") a catalyst composition is created. Thus, in another embodiment, the invention is a catalyst composition comprising the reaction product of: (a) A metal complex having the formula $LMXZ_n$ wherein X is selected from the group consisting of halides, hydride, triflate, acetates, borates, C_1 through C_{12} alkyl, C_1 through C_{12} alkoxy, C_3 through C_{12} cycloalkyl,

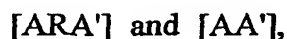
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C₃ through C₁₂ cycloalkoxy, aryl, thiolates, carbon monoxide, cyanate, olefins, and any other moiety into which a monomer can insert; M is selected from the group consisting of Cu, Ag, and Au; L is a nitrogen-containing bidentate ligand with more than two nitrogen atoms; Z is a neutral coordinating ligand; where n equals 0, 1, or 2; and (b) an activating cocatalyst.

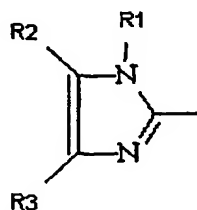
Furthermore, by controlling the temperature, catalyst loading, ligand structure, and residence time, product selectivity can be adjusted to produce individual polymers and copolymers with high selectivity. Hence, in yet another embodiment, the invention provides a method for producing polymers and copolymers.

Ideally, Z is weakly coordinating and sufficiently labile to allow activation of the catalyst. In a preferred embodiment composition, for each occurrence of Z, each Z is independently selected from the group consisting of diethylether, tetrahydrofuran, acetonitrile, benzonitrile, dioxane, acetone, 2-butanone, phenylisocyanate, ethylene, carbon monoxide, 1-hexene, and norbornene.

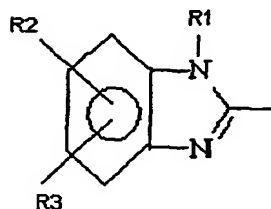
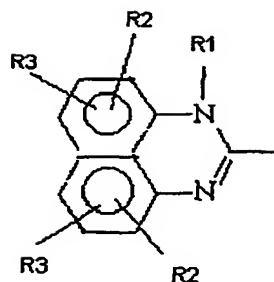
In another preferred embodiment of this invention is a complex having the formula LM_nZ_n, as described above, where L is a nitrogen-containing bidentate ligand represented by the formula:



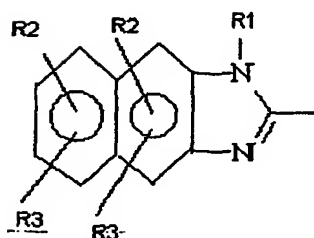
wherein A and A' are independently selected from the group consisting of



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, and



wherein R1 is independently selected from the group consisting of hydrogen, C₁ through C₁₂ straight chain or branched alkyl, C₃ through C₁₂ cycloalkyl, aryl, and trifluoroethane;

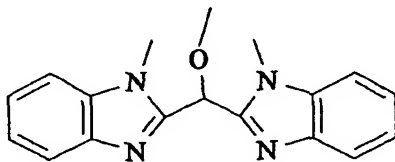
R2 and R3 are independently selected from the group consisting of hydrogen, C₁ through C₁₂ straight chain or branched alkyl, C₃ through C₁₂ cycloalkyl, C₁ through C₁₂ alkoxy, F, Cl, SO₃, C₁ through C₁₂ perfluoroalkyl, and N(CH₃)₂;

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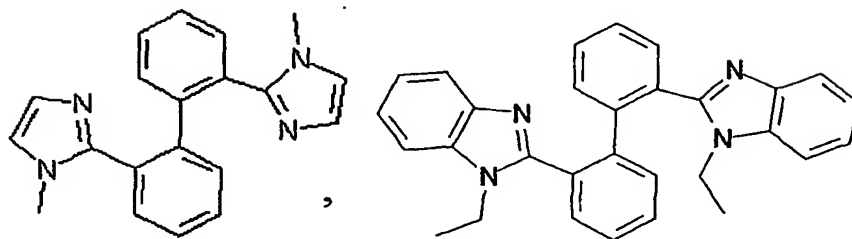
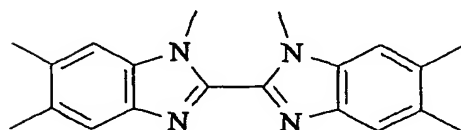
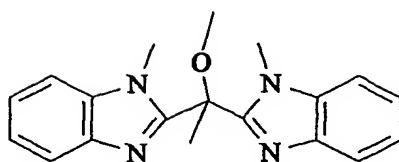
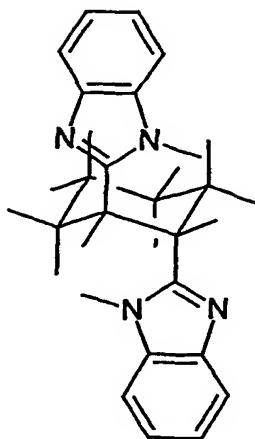
R is selected from the group consisting of non-substituted C₁ through C₁₂ alkyl, C₃ through C₁₂ cycloalkyl; methoxy; amino; halo; C₁ through C₁₂ haloalkyl substituted alkyl; cycloalkyl of up to 12 carbon atoms, C₁-C₄₀ aryl; and C₁-C₄₀ alkylaryl.

X is selected from the group consisting of halogens, hydride, triflate, acetate, trifluoroacetate, perfluorotetraphenylborate, tetrafluoroborate, C₁ through C₁₂ alkyl, C₁ through C₁₂ alkoxy, C₃ through C₁₂ cycloalkyl, C₃ through C₁₂ cycloalkoxy, aryl, and any other moiety into which a monomer can insert such as an atom, or group of atoms, covalently or ionically bonded to M; Z is a neutral coordinating ligand; where n equals 0, 1, or 2. In a preferred embodiment, for each occurrence of Z, each Z is independently selected from the group consisting of diethylether, tetrahydrofuran, acetonitrile, benzonitrile, dioxane, acetone, 2-butanone, phenylisocyanate, ethylene, carbon monoxide, 1-hexene, and norbornene.

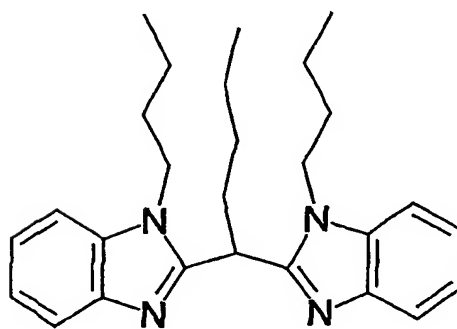
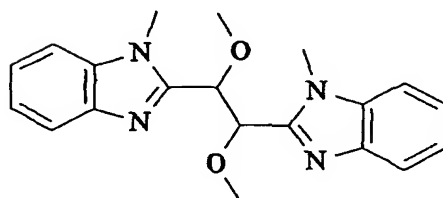
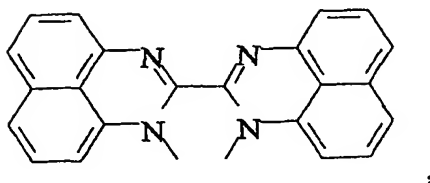
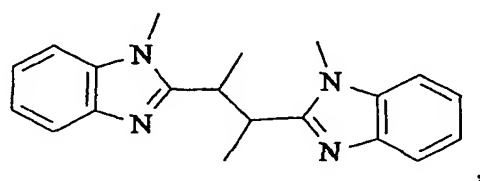
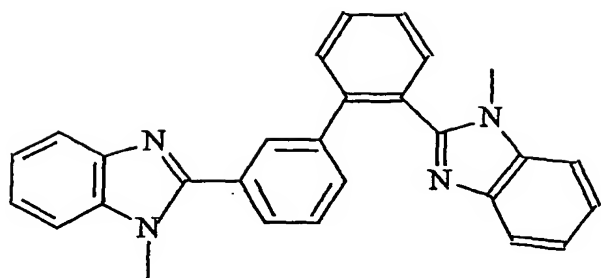
Accordingly, some of the ligands of the present invention have the following structures:



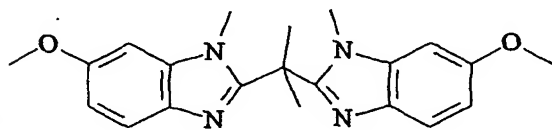
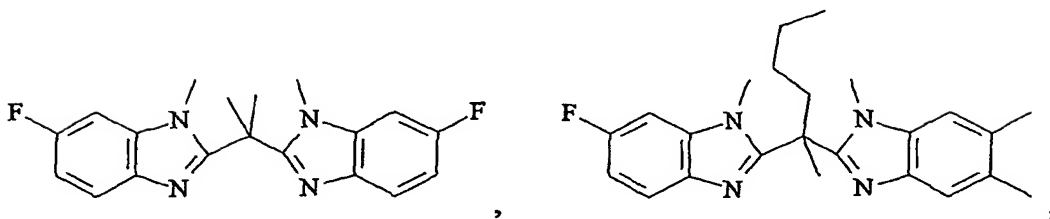
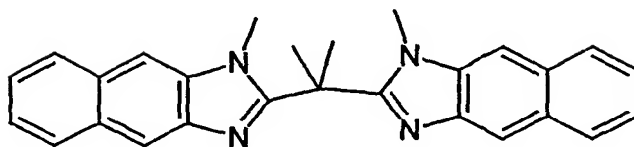
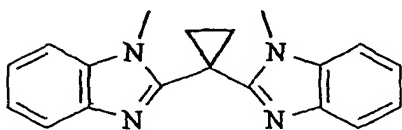
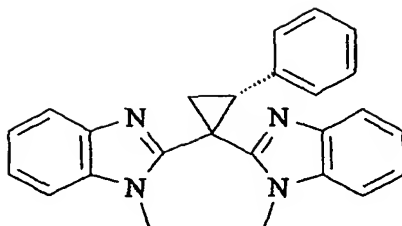
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, and

. For compactness, some bonds

are shown without termination; these bonds are terminated by methyl groups.

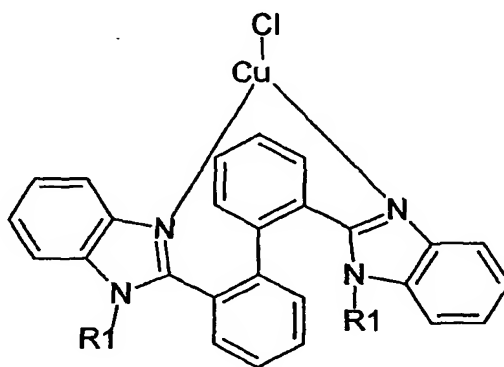
Cu is preferred for M. Among the options for X, halogens are preferred. Suitable non-halide options for X include, but are not limited to, triflate, trifluoroacetate, perfluorotetraphenyl borate, or tetrafluoro borate, hydride, alkyl

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groups or any other ligand into which a monomer can insert such as an atom, or group of atoms, covalently or ionically bonded to M.

Among the metal complexes of the present invention, particularly preferred embodiments are those having the 2,2' bis[2-(1-alkylbenzimidazol-2yl)] biphenyl, where the alkyl group is from C₁-C₂₀, and for X is chloride.

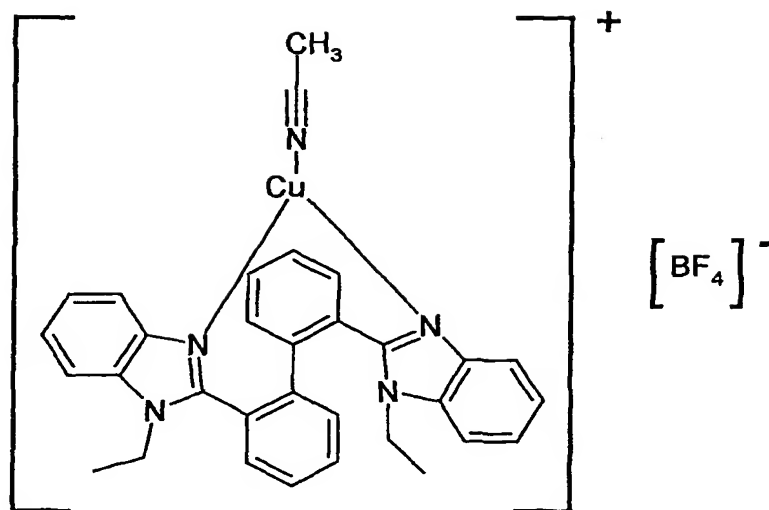
Generally, the 2,2'-bis[2-(1-alkylbenzimidazol-2yl)]biphenyl ligands having copper as the metal and chlorine as X, and C₁-C₂₀ as R₁, have the structure



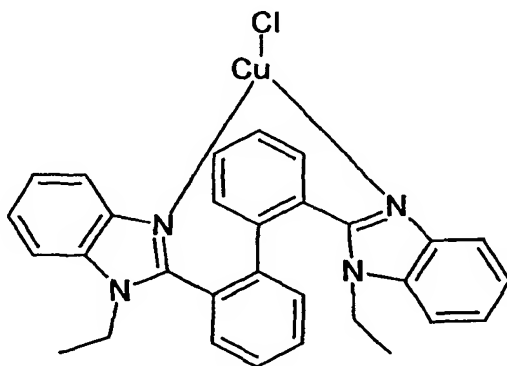
Preferred embodiments of specific metal complexes include, but are not limited to, the following:

[(2,2'-bis[2-(1-ethylbenzimidazol-2yl)]biphenyl)(acetonitrile)copper(I)]
(tetrafluoroborate)

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, and (2,2'-bis[2-(1-ethylbenzimidazol-2-yl)]biphenyl)copper(I)chloride



Advantageously, the catalysts of the present invention are not poisoned by compounds containing hydrocarbyl polar functional groups when used in the formation of polymers and copolymers synthesized all or in part from olefinic monomers. As such, the catalysts of the present invention are useful in preparing polymers and copolymers formed from olefinic monomers, such as polyethylene; polymers and copolymers formed from monomers containing hydrocarbyl polar functional groups such as poly(methyl methacrylate); and

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copolymers derived from olefins and monomers containing hydrocarbyl polar functional groups such as poly (ethylene-co-methyl methacrylate).

The activating cocatalysts used in conjunction with the metal complex defined above include, but are not limited to, aluminum compounds containing an Al-O bond such as the alkylalumoxanes such as methylalumoxane ("MAO"), isobutyl modified methylalumoxane ("MMAO"); "dry" [i.e., solvent free and Me_3Al ("TMA") free] MAO; aluminum alkyls; aluminum halides; alkyl-aluminum halides; Lewis acids other than any of the foregoing list; and mixtures of the foregoing can also be used in conjunction with alkylating agents, such as methyl magnesium chloride and methyl lithium. Examples of such Lewis acids are those compounds corresponding to the formula: $\text{R}^{\text{""}}_3\text{B}$, or $\text{R}_3^{\text{""}}\text{Al}$ wherein $\text{R}^{\text{""}}$ independently each occurrence is selected from hydrogen, silyl, hydrocarbyl, halohydrocarbyl, alkoxide, aryloxy, amide or combinations thereof, said $\text{R}^{\text{""}}$ having up to 30 nonhydrogen atoms.

It is to be appreciated by those skilled in the art, that the above formula for the preferred Lewis acids represents an empirical formula, and that many Lewis acids exist as dimers or higher oligomers in solution or in the solid state. Other Lewis acids which are useful in the catalyst compositions of this invention will be apparent to those skilled in the art.

Other examples of such cocatalysts include salts of group 13 element complexes. These and other examples of suitable cocatalysts and their use in organometallic polymerization are discussed in U. S. Patent No. 5,198,401 and PCT patent documents PCT/US97/10418 and PCT/US96/09764, all incorporated by reference herein.

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Preferred activating cocatalysts include trimethylaluminum, triisobutylaluminum, methylalumoxane, alkyl modified alumoxanes, "dry" alumoxanes, chlorodiethylaluminum, dichloroethylaluminum, triethylboron, trimethylboron, triphenylboron and halogenated, especially fluorinated, triaryl boron and aluminum compounds, carboranes and halogenated carboranes.

Most highly preferred activating cocatalysts include triethylaluminum, methylalumoxane, and fluoro-substituted aryl boranes and borates such as tris(4-fluorophenyl)boron, tris(2,4-difluorophenyl)boron, tris(3,5-bis(trifluoromethyl)phenyl) boron, tris(pentafluorophenyl) boron, pentafluorophenyl-diphenyl boron, and bis(pentafluorophenyl) phenylboron and tetrakis (pentafluorophenyl) borate. Such fluoro-substituted arylboranes may be readily synthesized according to techniques such as those disclosed in Marks, et al., J. Am. Chem. Soc., 113, 3623-3625 (1991). Fluorinated tetraaryl borates or aluminates and perfluoro tetranaphthyl borates or aluminates, are also well known in the art.

The catalyst can be utilized by forming the metal complex $LMXZ_n$, as defined above, and where required combining the activating cocatalyst with the same in a diluent. Optionally, an oxidizing agent may also be utilized in conjunction with the cocatalyst. Oxidizing agents may include, but are not limited to: $NOBF_4$; 1,4-benzoquinone; tetrachloro-1,4-benzoquinone; $AgClO_4$; $Ag(C_6F_5)_4B$; ferricinium $(C_6F_5)_4B$; $(3, 5(CF_3)_2(C_6H_4)B)Cp_2Fe^+$; and $(3, 5(CF_3)_2(C_6H_4)B)Cp_2^*Fe^+$. The preparation may be conducted in the presence of one or more addition polymerizable monomers, if desired. Preferably, the catalysts are prepared at a temperature within the range from $-100^\circ C.$ to $300^\circ C.$, preferably $0^\circ C$ to $250^\circ C$, most preferably $0^\circ C$ to $100^\circ C$. Suitable solvents include liquid or supercritical gases such as CO_2 , straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane,

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cycloheptane, methylcyclohexane, methylcycloheptane, halogenated hydrocarbons such as chlorobenzene, and dichlorobenzene perfluorinated C₄₋₁₀ alkanes and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and 4-vinylcyclohexane, (including all isomers alone or in mixtures). Other solvents include anisole, methylchloride, methylene chloride, 2-pyrrolidone and N-methylpyrrolidone. Preferred solvents are aliphatic hydrocarbons and aromatic hydrocarbon, such as toluene.

When an activating cocatalyst is used to form the catalyst composition, the equivalent ratio of metal complex to activating cocatalyst is preferably in a range from 1:0.5 to 1:10⁴, more preferably from 1:0.75 to 1:10³. In most polymerization reactions the equivalent ratio of catalyst:polymerizable compound employed is from 10⁻¹²: to 10⁻¹:1, more preferably from 10⁻⁹:1 to 10⁻⁴:1.

Olefinic monomers useful in the forming homopolymers and copolymers with the catalyst of the invention include, but are not limited to, ethylenically unsaturated monomers, nonconjugated dienes, and oligomers, and higher molecular weight, vinyl-terminated macromers. Examples include C₂₋₂₀ olefins, vinylcyclohexane, tetrafluoroethylene, and mixtures thereof. Preferred monomers include the C₂₋₁₀ α -olefins especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene or mixtures of the same.

Monomers having hydrocarbyl polar functional groups useful in forming homo and copolymers with the catalyst of the invention, are vinyl ether and C₁

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to C₂₀ alkyl vinyl ethers such as *n*-butyl vinyl ether, acrylates, such as C₁ to C₂₄, or alkyl acrylates such as *t*-butyl acrylate, and lauryl acrylate, as well as methacrylates such as methyl methacrylate.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from -100°C to 250°C preferably 0°C to 250°C, and pressures from atmospheric to 2000 atmospheres (200 Mpa). Suitable polymerization conditions include those known to be useful for metallocene catalyst when activated by aluminum or boron-activated compounds. Suspension, solution, slurry, gas phase or other process condition may be employed if desired. The catalyst may be supported and such supported catalyst may be employed in the polymerizations of this invention. Preferred supports include alumina, silica, polymeric supports and meso-porous materials.

The polymerization typically will be conducted in the presence of a solvent. Suitable solvents include those previously described as useful in the preparation of the catalyst. Indeed, the polymerization may be conducted in the same solvent used in preparing the catalyst. Optionally, of course, the catalyst may be separately prepared in one solvent and used in another.

The polymerization will be conducted for a time sufficient to form the polymer and the polymer is recovered by techniques well known in the art and illustrated in the following non-limiting examples which help to further described the invention.

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Example 1 - Preparation of [Cu(diEtBBIL)(ACN)](BF₄)

In an argon glovebox a colorless solution of 35 mg (0.11 mmol) of Cu(ACN)₄(BF₄) in 8 mL of acetonitrile was prepared. Then, 50 mg (0.11 mmol) of diEtBBIL was added to the solution and thoroughly mixed. The flask containing the colorless solution was then placed in a sealed jar containing diethylether to allow vapor diffusion. After one day colorless crystals of rac-[(2,2'-bis[2-(1-ethylbenzimidazol-2-yl)]biphenyl)(acetonitrile)copper(I)](tetrafluoroborate) were obtained. ¹H NMR (CDCl₃): δ = 7.65(d, J = 6,7 Hz, 2H), 7.54(dd, J = 7.8 Hz, J = 17.9 Hz, 4H), 7.33(m, 8H), 6.93(d, J = 7,4 Hz, 2H), 4.47(dm, J = 40.3 Hz, 4H), 2.15(s, 3H), 1.66(t, J = 6.8 Hz, 6H). X-ray crystallographic data: monoclinic, P2(1), Z = 4, a = 16.952(3), b = 15.527(3), c = 12.946(2), α = 90, β = 111.33(3), γ = 90, V = 3174.15.

Example 2 - Preparation of Cu(I)(diEtBBIL)Cl by reduction

A 100 mg quantity of 10 μ copper powder was placed in a 100 mL round bottom flask with a side arm. Then, 2 mL of triethylorthoformate and 20 mL of acetonitrile were added to the flask. The flask was fitted with bubbler and was degassed under a continuous flow of nitrogen. Then, 33 mg (0.19 mmol) of CuCl₂•2 H₂O was added to the stirring mixture under a positive flow of nitrogen to give a green solution. Then, 170 mg (0.38 mmol) of diEtBBIL was added to the flask to give a yellow solution. The mixture was stirred under nitrogen for more than 72 hours. The flask containing the colorless solution and remaining solid was then filtered to give a colorless filtrate. The solvent was removed under a flow of nitrogen to give a white solid. The solid was placed under high vacuum an additional hour to give 144 mg of white (2,2'-bis[2-(1-ethylbenzimidazol-2-yl)]biphenyl)copper(I)chloride. ¹H NMR (CDCl₃): δ =

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8.08(m, 2H), 7.69(m, 1H), 7.53(m, 3H), 7.27(m, 6H), 6.95(dm, 4H), 4.38(dm, 4H), 1.58(m, 3H), 1.90(m, 3H).

Example 3 - Preparation of Polyethylene Using [Cu(I)(diEtBBIL)(ACN)](BF₄)

A 32.1 mg (0.051 mmol) quantity of Cu(diEtBBIL)(MeCN)BF₄ was weighed out in a glass liner under argon. Then, 30 mL of toluene was added to the liner, followed by 2.0 g of 30 wt. % MAO (0.010 mol) resulting in a pale yellow slurry. The liner was placed in a 300 mL Parr reactor which was sealed, pressurized with ethylene and heated to 80°C. The reaction was run for 15 hours at 720 psig. At the end of this time period, the reactor was cooled, vented and quenched with 5 mL of methanol. Then the polymer was precipitated out in 150 mL of acidic methanol (10%). The polymer was isolated by filtration and dried under vacuum at 50°C for a day. Yield: 0.8 g. T_m: 142°C (second heat). ¹³C NMR (ppm, 125°C tetrachloroethane): 29.5 (s, -CH₂-CH₂-); no evidence of end groups and branch points up to the detection limits of about one carbon per 500-1000 carbons.

Example 4 - Preparation of Poly(*t*-butyl acrylate) Using [Cu(I)(diEtBBIL)(ACN)](BF₄)

A 32.1 mg (0.051 mmol) quantity of Cu(diEtBBIL)(MeCN)BF₄ was added to a 100 mL round-bottomed flask in an argon glovebox. 10 mL of toluene was added to the flask, followed by 1.02 g of 30 wt. % MAO (5.3 mmol) resulting in an yellow slurry. 5.9 g of *t*-butyl acrylate (freshly distilled from CaCl₂ and stabilized with 300 ppm of phenathiazine) was added to the slurry. The slurry was allowed to stir at room temperature for 18 hours in the dark. At the end of this time period, the reaction was quenched with 5 mL of methanol and then the polymer was precipitated out in 150 mL of acidic methanol (10%). The polymer was isolated by filtration and dried under vacuum at 40°C for a

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day. Yield : 14 %. ^{13}C NMR (ppm, CDCl_3): 28.2 (s, $-\text{CH}_2-$ CH($\text{COOC}(\text{CH}_3)_3$)-), 34.3-37.6 (m, $-\text{CH}_2-\text{CH}(\text{COOC}(\text{CH}_3)_3)$ -), 42-43.5 (m, $-\text{CH}_2-\text{CH}(\text{COOC}(\text{CH}_3)_3)$ -), 80.5 (m, $-\text{CH}_2-\text{CH}(\text{COOC}(\text{CH}_3)_3)$ -), 173.2-174.1 (m, $-\text{CH}_2-\text{CH}(\text{COOC}(\text{CH}_3)_3)$ -), 39%*orr*, 47% *mr*, 14% *mm* (by integration of methine peak).

Example 5 - Preparation of Polyethylene Using $[\text{Cu}(\text{I})(\text{diEtBBIL})(\text{ACN})](\text{BF}_4)$

The polymerization was run using a mixture prepared by dissolving 21.1 mg (0.033 mmol) of $[\text{Cu}(\text{diEtBBIL})(\text{ACN})](\text{BF}_4)$ in 80 ml of toluene to give a colorless solution. This was followed by the addition of 100 mg of NOBF_4 (0.85 mmol) maintaining a colorless solution. This was followed by the addition of 1.5 ml of 30% MAO to give an intense yellow solution. The Parr reactor was pressurized with 550 psig of ethylene and heated to 80°C and maintained at 80°C for 20.75 hours during which the pressure dropped from 560 psig to 540 psig. The polymerization mixture was cooled and quenched with methanol to give 31 mg of solid polyethylene upon workup.

Example 6 - Preparation of Poly(*t*-butyl acrylate-ethylene)

A 24.1 mg (0.045 mmol) quantity of $\text{Cu}(\text{diEtBBIL})\text{Cl}$ was weighed out in a glass liner under argon. 30 mL of toluene was added to the liner, followed by 1.98 g of 30 wt. % MAO (0.010 mol) resulting in a pale yellow slurry. Next, 10.7 grams of *t*-butyl acrylate (*t*-butyl acrylate was distilled from CaCl_2 , degassed and taken into the glove box, then approximately 100 ppm phenathiazine was added) was added to the slurry. The liner was placed in a 300 mL Parr reactor which was sealed, pressurized with ethylene and heated to 80°C . The reaction was run for 17 hours at 840 psig. At the end of this time period, the reactor was cooled, vented and quenched with 5 mL of methanol and then the

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polymer was precipitated out in 300 mL of acidic methanol (10 %). The polymer was isolated by filtration and dried under vacuum at 60°C for a day. The yield was 4.5 g. The polymer was extracted in THF in a soxhlet extractor to remove any catalyst residue and characterized.

The composition of the copolymers was determined by ^{13}C -NMR in CDCl_3 . The acrylate ester content was calculated by averaging the integral values for the acrylate carbonyl and quarternary carbon of *t*-butyl group. Ethylene content is then obtained by correcting the total aliphatic integral for the *t*-butyl acrylate integration. Furthermore, acrylate-centered traits were quantified by integration of three clusters of methine resonances: EAE : 46.5, EAA/AAE: 44.2, AAA: 42.2 ppm. The copolymer was found to have 76 mol% *t*-butyl acrylate with EAE:EAA/AAE:AAA = 8:38:53.

The foregoing examples clearly demonstrate that the novel composition of the instant invention can be used as an effective polymerization catalyst to make polymers and copolymers including copolymers having polar functionality. More specifically, the examples show how polar monomers can be readily-polymerized without poisoning the catalyst. Also, the chain, as opposed to the branches, contain a significant quantity of the polar monomer(s). Furthermore, the polymers formed are not highly branched. Additionally, the examples show that the polymers formed have a high percent of polar monomer content (e.g., greater than about 15 mol%). Finally, there are a variety of polar monomers which may be incorporated into the olefinic polymer and copolymer products. These features overcome the disadvantages of the most organo-metallic catalyst technology used today as discussed above in the background section.

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CLAIMS:

1. A composition comprising the formula $LMXZ_n$, wherein X is selected from the group consisting of halides, hydride, triflate, acetates, borates, C_1 through C_{12} alkyl, C_1 through C_{12} alkoxy, C_3 through C_{12} cycloalkyl, C_3 through C_{12} cycloalkoxy, aryl, thiolates, carbon monoxide, cyanate, olefins, and any other moiety into which a monomer can insert; M is selected from the group consisting of Cu, Ag, and Au; L is a nitrogen-containing bidentate ligand with more than two nitrogen atoms; Z is a neutral coordinating ligand; wherein n equals 0, 1, or 2.
2. The composition according to claim 1 wherein for each occurrence of Z, each Z is independently selected from the group consisting of diethylether, tetrahydrofuran, acetonitrile, benzonitrile, dioxane, acetone, 2-butanone, phenylisocyanate, ethylene, carbon monoxide, 1-hexene, and norbornene.
3. A catalyst composition comprising the reaction product of:
 - (a) A metal complex having the formula $LMXZ_n$ wherein X is selected from the group consisting of halides, hydride, triflate, acetates, borates, C_1 through C_{12} alkyl, C_1 through C_{12} alkoxy, C_3 through C_{12} cycloalkyl, C_3 through C_{12} cycloalkoxy, aryl, thiolates, carbon monoxide, cyanate, olefins, and any other moiety into which a monomer can insert; M is selected from the group consisting of Cu, Ag, and Au; L is a nitrogen-containing bidentate ligand having more than two nitrogen atoms; Z is a neutral coordinating ligand; wherein n equals 0, 1, or 2; and
 - (b) an activating cocatalyst.
4. The composition according to claim 3 wherein M is Cu.

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5. The composition according to claim 3 wherein for each occurrence of Z, each Z is independently selected from the group consisting of diethylether, tetrahydrofuran, acetonitrile, benzonitrile, dioxane, acetone, 2-butanone, phenylisocyanate, ethylene, carbon monoxide, 1-hexene, and norbornene.

6. The composition according to claim 3 wherein the activating cocatalyst is methyl alumoxane.

7. A method for polymerizing olefinic monomers selected from the group consisting of: (a) acyclic aliphatic olefins, (b) olefins having a hydrocarbyl polar functionality and (c) mixtures of (i) at least one olefin having a hydrocarbyl polar functional group and (ii) at least one acyclic aliphatic olefin, the method comprising contacting the olefinic monomers under polymerization conditions with a catalyst composition comprising the reaction product of: (a) A metal complex having the formula $LMXZ_n$ wherein X is selected from the group consisting of halides, hydride, triflate, acetates, borates, C_1 through C_{12} alkyl, C_1 through C_{12} alkoxy, C_3 through C_{12} cycloalkyl, C_3 through C_{12} cycloalkoxy, aryl, thiolates, carbon monoxide, cyanate, olefins, and any other moiety into which a monomer can insert; M is selected from the group consisting of Cu, Ag, and Au; L is a nitrogen-containing bidentate ligand with more than two nitrogen atoms; Z is a neutral coordinating ligand; wherein n equals 0, 1, or 2; and (b) an activating cocatalyst.

8. The method according to claim 7 further comprising contacting said metal complex with an oxidizing agent.

9. The composition according to claim 7 wherein for each occurrence of Z, each Z is independently selected from the group consisting of diethylether,

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tetrahydrofuran, acetonitrile, benzonitrile, dioxane, acetone, 2-butanone, phenylisocyanate, ethylene, carbon monoxide, 1-hexene, and norbornene.

10. The composition according to claim 7 wherein the activating cocatalyst is methyl alumoxane.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/24290

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F1/08 C08F110/02 C08F4/54 C08F10/00 C08F4/52
C08F210/02 B01J31/14 B01J31/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C08F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 30822 A (EXXON RESEARCH ENGINEERING CO) 24 June 1999 (1999-06-24) cited in the application page 12 -page 23	1,3,7
X	USON, R. ET AL: "New ways for the preparation of heterocyclic gold(III) complexes" J. ORGANOMET. CHEM., vol. 209, no. 2, 1981, pages 271-279, XP001031111 page 273 --- -/--	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/24290

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SUN, WEI-YIN ET AL: "Synthesis and crystal structure of three-coordinated silver(I) and copper(I) complexes with N2P binding set containing a novel tripodal ligand: 1,3,5-tris(benzimidazol-2-ylmethyl)benzene " NEW J. CHEM., vol. 24, no. 7, 2000, pages 519-522, XP001039628 the whole document	1,2
X	GORUN, SERGIU M. ET AL: "Benzimidazol-2-ylcarbinols and Benzimidazol-2-yl Ketones: Novel Bifunctional Chelating Ligands for Copper" INORG. CHEM., vol. 35, no. 1, 1996, pages 3-4, XP001039629 the whole document	1,2
X	DE SOUZA LEMOS, S. ET AL: "Preparation and crystal structures of neutral and cationic copper(I) mixed ligand complexes with triphenylphosphine and derivatives of biimidazole" Z. ANORG. ALLG. CHEM., vol. 624, no. 4, 1998, pages 701-707, XP001039635 page 702	1,2
X	BERNARDINELLI, GERALD ET AL: "Complexes of copper with a flexible bisbenzimidazole ligand" CHIMIA, vol. 46, no. 4, 1992, pages 155-158, XP001035962 page 156	1,2

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-10 (all partially not searched)

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim(s) may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claim(s) is impossible. Consequently, the search has been restricted to:

Compounds according to claim 1 with $M=Cu$ and the ligand L being of the bisbenzimidazol-yl biphenyl type as depicted on page 8, 9, 11,12 and as used throughout the examples.

Consequently also the catalyst composition of claim 3, the method of claim 7 and the composition according to claim 9 have been searched only with respect to the aforementioned restrictions.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT
 information on patent family members

International Application No
PCT/US 01/24290

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9930822 A	24-06-1999	AU 1916099 A	05-07-1999
		EP 1017491 A1	12-07-2000
		WO 9930822 A1	24-06-1999
		US 6037297 A	14-03-2000
		US 6180788 B1	30-01-2001
